BLEACHED CROSSLINKED CELLULOSIC FIBERS HAVING HIGH COLOR AND RELATED METHODS

FIELD OF THE INVENTION

The present invention relates to whitened crosslinked cellulosic fibers and methods for making and using whitened crosslinked cellulosic fibers.

BACKGROUND OF THE INVENTION

Cellulosic fibers are a basic component of absorbent products such as diapers. These fibers form a liquid absorbent structure, a key functioning element in the absorbent product. Cellulosic fluff pulp, a form of cellulosic fibers, is a preferred fiber for this application because a high void volume or high bulk, liquid absorbent fiber structure is formed. This structure, however, tends to collapse on wetting. The collapse or reduction in fiber structure bulk reduces the volume of liquid which can be retained in the wetted structure and inhibits the wicking of liquid into the unwetted portion of the cellulose fiber structure. Consequently, the potential capacity of the dry high bulk fiber structure is never realized and it is the fiber structure's wet bulk which determines the liquid holding capacity of the overall fiber structure.

Fiber structures formed from crosslinked cellulosic fibers generally have enhanced wet bulk compared to those formed from uncrosslinked fibers. The enhanced bulk is a consequence of the stiffness, twist, and curl imparted to the fiber as a result of crosslinking. Accordingly, crosslinked fibers are advantageously incorporated into absorbent products to enhance their wet bulk.

Polycarboxylic acids have been used to crosslink cellulosic fibers. See, for example, U.S. Patent No. 5,137,537; U.S. Patent No. 5,183,707; and U.S. Patent No. 5,190,563. These references describe absorbent structures containing individualized

cellulosic fibers crosslinked with a C2-C9 polycarboxylic acid. Absorbent structures made from these individualized, crosslinked fibers exhibit increased dry and wet resilience and have improved responsiveness to wetting relative to structures containing uncrosslinked fibers. Furthermore, a preferred polycarboxylic crosslinking agent, citric acid, is available in large quantities at relatively low prices making it commercially competitive with formaldehyde and formaldehyde addition products.

Despite the advantages that polycarboxylic acid crosslinking agents provide, cellulosic fibers crosslinked with low molecular weight polycarboxylic acids such as citric acid, tend to lose their crosslinks over time and revert to uncrosslinked fibers. For example, citric acid crosslinked fibers show a considerable loss of crosslinks on storage. Such a reversion of crosslinking generally defeats the purpose of fiber crosslinking, which is to increase the fiber's bulk and capacity. Thus, the useful shelf-life of fibers crosslinked with these polycarboxylic acids is relatively short and renders the fibers somewhat limited in their utility. Polymeric polycarboxylic acid crosslinked fibers, however, exhibit a density that remains substantially unchanged over the life-time of fibrous webs prepared from these fibers. See, for example, U.S. Patent No. 6,620,865. This resistance to aging or reversion of density relates to the stable intrafiber crosslinks formed using polymeric polycarboxylic acid crosslinking agents. In contrast, cellulose fibers crosslinked with citric acid show a considerable increase in density, accompanied by a loss of bulk and absorbent capacity over time. Generally, the increase in density indicates a decrease in the level of crosslinking (i.e., reversion) in the fibers. In addition to density increase, the loss of crosslinking in the fibrous web results in a less bulky web and, consequently, diminished absorbent capacity and liquid acquisition capability.

Unfortunately, citric acid or polycarboxylic acid crosslinking agents can cause discoloration (i.e., yellowing) of the white cellulosic fibers at the elevated temperatures required to effect the crosslinking reaction.

Bleaching is a common method for increasing pulp brightness of pulp. Industry practice for improving appearance of fluff pulp is to bleach the pulp to ever-higher levels of brightness (the Technical Association of the Pulp & Paper Industry ("TAPPI") or the International Organization for Standardization ("ISO")). Traditional bleaching agents include elemental chlorine, chlorine dioxide, and hypochlorites. However, bleaching is expensive, environmentally harsh, and often a source of manufacturing bottleneck.

Widespread consumer preference for a brighter, whiter pulp drives manufacturers to pursue ever more aggressive bleaching strategies. While highly bleached pulps are "whiter" than their less-bleached cousins, these pulps are still yellow-white in color. A yellow-white product is undesirable. Countless studies suggest that consumers clearly favor a blue-white over a yellow-white color. The former is perceived to be whiter, i.e., "fresh", "new" and "clean", while the latter is judged to be "old", "faded", and "dirty".

In addition to fiber discoloration, unpleasant odors can also be associated with the use of α-hydroxy carboxylic acids such as citric acid. Recently, it was found that the characteristic odor associated with citric acid crosslinked cellulosic fibers could be removed and the brightness improved by contacting the fibers with an alkaline solution (e.g., an aqueous solution of sodium hydroxide) and an oxidizing bleaching agent (e.g., hydrogen peroxide). See U.S. Patent No. 5,562,740. In the method, the alkaline solution raises the finished fiber pH preferably to the 5.5-6.5 range from about 4.5. This, in combination with the oxidizing bleaching agent, eliminates the "smokey and burnt" odor characteristics of the citric acid crosslinked fibers. The oxidizing bleaching agent also helps to increase final product brightness.

The addition of small amounts of blue colorant to improve whiteness appearance is known in other fields, such as papermaking.

The practice of pre-coloring papermaking pulp is not usually done nor is it necessarily desired. The intentional alteration of pulp optical properties often ends up degrading product specifications, such as TAPPI brightness, which is undesirable. One runs the risk that colorants may not survive the unpredictable manufacturing environments of downstream processes. This is because previously applied colorant can be adversely affected chemically and/or physically during post-processing operations resulting in unexpected or undesirable color changes or even full loss of color. Furthermore, some colorants can be lost or rendered ineffective during various post-processing operations disrupting process health and reliability. Therefore, any optical enhancement is usually accomplished by addition of tinting colorants, fillers, and/or fluorescent dye during the papermaking stage.

A process for enhancing the whiteness, brightness, and chromaticity of papermaking fibers has been described in U.S. Patent No. 5,482,514. The process relates to adding photoactivators, particularly water-soluble phthalocyanines, to papermaking

fibers to enhance their optical properties by a catalytic photosensitizer bleaching process. The resulting bleached papermaking fibers can be advantageously incorporated into paper sheets.

While it is common in papermaking practice to boost whiteness properties, it is novel in the practice of making crosslinked cellulosic fibers.

Accordingly, there exists a need for crosslinked cellulosic fibers having improved whiteness. A need also exists for a method for making whitened crosslinked cellulosic fibers. The present invention seeks to fulfill these needs and provides further related advantages.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides whitened crosslinked cellulosic fibers. In one embodiment, the whitened crosslinked cellulosic fibers of the invention are cellulosic fibers that have been treated with a crosslinking agent and a whitening agent that includes one or more dyes, and then treated with a bleaching agent. In one embodiment, the whitened crosslinked cellulosic fibers are cellulosic fibers that have been treated with citric acid and a whitening agent that includes a blue dye, and then treated with an alkaline hydrogen peroxide solution. In another embodiment, the whitened crosslinked cellulosic fibers of the invention are cellulosic fibers that have been treated with a crosslinking agent and a whitening agent that includes one or more dyes.

In another aspect of the invention, methods for making whitened crosslinked cellulosic fibers are provided. In one method, cellulosic fibers are first treated with a crosslinking agent and a whitening agent that includes one or more dyes to provide dyed fibers that are then treated with a bleaching agent. In another method, cellulosic fibers are treated with a crosslinking agent and a whitening agent that includes one or more dyes to provide whitened fibers.

In other aspects, the invention provides absorbent products including wipes, towels, and tissues, as well as infant diapers, adult incontinence products, and feminine hygiene products that include whitened crosslinked cellulosic fibers.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In one aspect, the present invention provides whitened crosslinked cellulosic fibers. In one embodiment, the whitened crosslinked cellulosic fibers of the invention are cellulosic fibers that have been treated with a crosslinking agent, optional crosslinking

catalyst, and a whitening agent that includes one or more dyes, followed by treatment with a bleaching agent to provide crosslinked cellulosic fibers having high bulk and improved color (e.g., whiteness). In another embodiment, the whitened crosslinked cellulosic fibers of the invention are cellulosic fibers that have been treated with a crosslinking agent, optional crosslinking catalyst, and a whitening agent that includes one or more dyes to provide crosslinked cellulosic fibers having high bulk and improved color (e.g., whiteness).

The color improvement achieved by the crosslinked fibers of the invention results from treatment of the fibers with a whitening agent that includes one or more dyes. Additional color improvement results from subsequent treatment of the dyed crosslinked fibers with a bleaching agent.

In one embodiment, the whitening agent includes a blue dye. Representative blue dyes are commercially available from Ciba Specialty Chemicals, High Point, NC, under the designations Irgalite Blue RL, Irgalite Blue RM, Pergasol Blue PTD (formerly Pergasol Blue BVC), Pergasol Blue NLF, and Pergasol Blue 2R-Z; Levacel products from Bayer AG; and Cartasol products from Clariant. Suitable blue dyes include azo dyes and azo metal complex dyes. Pergasol Blue PTD and Pergasol Blue NLF are azo dyes. Pergasol Blue 2R-Z is an azo metal complex dye.

The whitened crosslinked cellulosic fibers of the invention include from about 2.84 g dye per air-dried metric ton fiber (2.84 g/admt) to about 284 g dye/admt fiber. In one embodiment, the fibers include from about 2.84 g dye/admt fiber to about 142 g dye/admt fiber, and in another embodiment, from about 2.84 g dye/admt fiber to about 85 g dye/admt fiber.

Any one of a number of crosslinking agents and crosslinking catalysts, if necessary, can be used in making the whitened crosslinked cellulosic fibers of the present invention. The following is a representative list of useful crosslinking agents and catalysts. Each of the noted patents is expressly incorporated herein by reference in its entirety.

Suitable urea-based crosslinking agents include substituted ureas such as methylolated ureas, methylolated cyclic ureas, methylolated lower alkyl cyclic ureas, methylolated dihydroxy cyclic ureas, dihydroxy cyclic ureas, and lower alkyl substituted cyclic ureas. Specific urea-based crosslinking agents include dimethyldihydroxy urea

(DMDHU, 1,3-dimethyl-4,5-dihydroxy-2-imidazolidinone), dimethyloldihydroxyethylene urea (DMDHEU, 1,3-dihydroxymethyl-4,5-dihydroxy-2-imidazolidinone), dimethylol urea (DMU, bis[N-hydroxymethyl]urea), dihydroxyethylene urea (DHEU, 4,5-dihydroxy-2-imidazolidinone), dimethylolethylene urea (DMEU, 1,3-dihydroxymethyl-2-imidazolidinone), and dimethyldihydroxyethylene urea (DMeDHEU or DDI, 4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone).

Suitable crosslinking agents include dialdehydes such as C_2-C_8 dialdehydes (e.g., glyoxal), C_2-C_8 dialdehyde acid analogs having at least one aldehyde group, and oligomers of these aldehyde and dialdehyde acid analogs, as described in U.S. Patent Nos. 4,822,453; 4,888,093; 4,889,595; 4,889,596; 4,889,597; and 4,898,642. Other suitable dialdehyde crosslinking agents include those described in U.S. Patent Nos. 4,853,086; 4,900,324; and 5,843,061.

Other suitable crosslinking agents include aldehyde and urea-based formaldehyde addition products. See, for example, U.S. Patent Nos. 3,224,926; 3,241,533; 3,932,209; 4,035,147; 3,756,913; 4,689,118; 4,822,453; 3,440,135; 4,935,022; 3,819,470; and 3,658,613.

Suitable crosslinking agents include glyoxal adducts of ureas, for example, U.S. Patent No. 4,968,774, and glyoxal/cyclic urea adducts as described in U.S. Patent Nos. 4,285,690; 4,332,586; 4,396,391; 4,455,416; and 4,505,712.

Other suitable crosslinking agents include carboxylic acid crosslinking agents such as polycarboxylic acids. Polycarboxylic acid crosslinking agents (e.g., citric acid, propane tricarboxylic acid, and butane tetracarboxylic acid) and catalysts are described in U.S. Patent Nos. 3,526,048; 4,820,307; 4,936,865; 4,975,209; and 5,221,285. The use of C_2-C_9 polycarboxylic acids that contain at least three carboxyl groups (e.g., citric acid and oxydisuccinic acid) as crosslinking agents is described in U.S. Patent Nos. 5,137,537; 5,183,707; 5,190,563; 5,562,740, and 5,873,979.

Polymeric polycarboxylic acids are also suitable crosslinking agents. Suitable polymeric polycarboxylic acid crosslinking agents are described in U.S. Patent Nos. 4,391,878; 4,420,368; 4,431,481; 5,049,235; 5,160,789; 5,442,899; 5,698,074; 5,496,476; 5,496,477; 5,728,771; 5,705,475; and 5,981,739. Polyacrylic acid and related copolymers as crosslinking agents are described U.S. Patent Nos. 5,549,791, 5,998,511,

and 6,306,251. Polymaleic acid crosslinking agents are described in U.S. Patent No. 5,998,511.

Specific suitable polycarboxylic acid crosslinking agents include citric acid, tartaric acid, malic acid, succinic acid, glutaric acid, citraconic acid, itaconic acid, tartrate monosuccinic acid, maleic acid, polyacrylic acid, polymethacrylic acid, polymaleic acid, polymethylvinylether-co-maleate copolymer, polymethylvinylether-co-itaconate copolymer, copolymers of acrylic acid, and copolymers of maleic acid.

Other suitable crosslinking agents are described in U.S. Patent Nos. 5,225,047; 5,366,591; 5,556,976; and 5,536,369.

In one embodiment, the crosslinking agent is citric acid.

Suitable crosslinking catalysts can include acidic salts, such as ammonium chloride, ammonium sulfate, aluminum chloride, magnesium chloride, magnesium nitrate, and alkali metal salts of phosphorous-containing acids. In one embodiment, the crosslinking catalyst is sodium hypophosphite. The amount of crosslinking catalyst used can vary from about 0.1 to about 5 percent by weight based in the total weight of dry fibers.

Mixtures or blends of crosslinking agents and catalysts can also be used in making the crosslinked fibers of the invention.

The crosslinking agent is applied to the cellulosic fibers in an amount sufficient to effect intrafiber crosslinking. The amount applied to the cellulosic fibers can be from about 1 to about 10 percent by weight based on the total weight of dry fibers. In one embodiment, crosslinking agent in an amount from about 4 to about 6 percent by weight based on the total weight of dry fibers.

In one embodiment, the whitened crosslinked cellulosic fibers of the invention are whitened citric acid crosslinked cellulosic fibers.

Although available from other sources, cellulosic fibers useful for making the crosslinked cellulosic fibers useful in making the whitened crosslinked cellulosic fibers of the invention are derived primarily from wood pulp. Suitable wood pulp fibers for use with the invention can be obtained from well-known chemical processes such as the kraft and sulfite processes, with or without subsequent bleaching. The pulp fibers may also be processed by thermomechanical, chemithermomechanical methods, or combinations thereof. The preferred pulp fiber is produced by chemical methods. Ground wood fibers,

recycled or secondary wood pulp fibers, and bleached and unbleached wood pulp fibers can be used. The preferred starting material is prepared from long-fiber coniferous wood species, such as southern pine, Douglas fir, spruce, and hemlock. Details of the production of wood pulp fibers are well-known to those skilled in the art. These fibers are commercially available from a number of companies, including Weyerhaeuser Company. For example, suitable cellulose fibers produced from southern pine that are usable with the present invention are available from Weyerhaeuser Company under the designations CF416, CF405, NF405, PL416, FR416, FR516, and NB416.

The wood pulp fibers useful in the present invention can also be pretreated prior to use with the present invention. This pretreatment may include physical treatment, such as subjecting the fibers to steam or chemical treatment. Although not to be construed as a limitation, examples of pretreating fibers include the application of fire retardants to the fibers, and surfactants or other liquids, such as solvents, which modify the surface chemistry of the fibers. Other pretreatments include incorporation of antimicrobials, pigments, and densification or softening agents. Fibers pretreated with other chemicals, such as thermoplastic and thermosetting resins also may be used. Combinations of pretreatments also may be employed.

In another aspect of the invention, methods for making whitened crosslinked cellulosic fibers are provided. In one method, cellulosic fibers are treated with one or more dyes, one or more crosslinking agents, and optionally one or more crosslinking catalysts to provide dyed crosslinked fibers that are subsequently treated with a bleaching agent to provide crosslinked cellulosic fibers having improved color. In another method, cellulosic fibers are treated with one or more dyes, one or more crosslinking agents, and optionally one or more crosslinking catalysts to provide dyed crosslinked having improved color.

The whitened crosslinked cellulose fibers of the invention can be prepared by a system and apparatus as described in U.S. Patent No. 5,447,977 to Young, Sr. et al., expressly incorporated herein by reference in its entirety. Briefly, the fibers are prepared by a system and apparatus that includes a conveying device for transporting a mat or web of cellulose fibers through a fiber treatment zone; an applicator for applying a treatment substance (e.g., whitening agent, crosslinking agent, and optional crosslinking catalyst) from a source to the fibers at the fiber treatment zone; a fiberizer for separating the

individual cellulose fibers comprising the mat to form a fiber output comprised of substantially unbroken and essentially singulated cellulose fibers; a dryer coupled to the fiberizer for flash evaporating residual moisture; and a controlled temperature zone for additional heating of fibers and an oven for curing the crosslinking agent, to form dried and cured individualized dyed, crosslinked fibers. In one embodiment of the method, the dyed fibers are then treated with a bleaching agent to provide the whitened crosslinked fibers.

As used herein, the term "mat" refers to any nonwoven sheet structure comprising cellulose fibers or other fibers that are not covalently bound together. The fibers include fibers obtained from wood pulp or other sources including cotton rag, hemp, grasses, cane, husks, cornstalks, or other suitable sources of cellulose fibers that may be laid into a sheet. The mat of cellulose fibers is preferably in an extended sheet form, and may be one of a number of baled sheets of discrete size or may be a continuous roll.

Each mat of cellulose fibers is transported by a conveying device, for example, a conveyor belt or a series of driven rollers. The conveying device carries the mats through the fiber treatment zone.

At the fiber treatment zone, a solution containing the whitening agent (e.g., one or more dyes), crosslinking agent, and optional crosslinking catalyst is applied to the mat of cellulose fibers. The solution is preferably applied to one or both surfaces of the mat using any one of a variety of methods known in the art, including spraying, rolling, or dipping. Once the solution has been applied to the mat, the solution may be uniformly distributed through the mat, for example, by passing the mat through a pair of rollers thereby impregnating the mat with the whitening agent, crosslinking agent, and optional crosslinking catalyst.

After the mat's fibers have been treated with the solution containing the whitening agent, crosslinking agent, and optional catalyst, the impregnated mat is fiberized by feeding the mat through a hammermill. The hammermill serves to disintegrate the mat into its component individual cellulose fibers, which are then air conveyed through a drying unit to remove the residual moisture. In a preferred embodiment, the fibrous mat is wet fiberized.

The resulting treated pulp is then air conveyed through an additional heating zone (e.g., a dryer) to bring the temperature of the pulp to the cure temperature. In one

embodiment, the dryer comprises a first drying zone for receiving the fibers and for removing residual moisture from the fibers via a flash-drying method, and a second heating zone for curing the crosslinking agent. Alternatively, in another embodiment, the treated fibers are blown through a flash-dryer to remove residual moisture, heated to a curing temperature, and then transferred to an oven where the treated fibers are subsequently cured. Overall, the treated fibers are dried and then cured for a sufficient time and at a sufficient temperature to effect crosslinking. Typically, the fibers are oven-dried and cured for about 1 to about 20 minutes at a temperature from about 120°C to about 165°C. The product of the process is dyed crosslinked cellulosic fibers having improved color properties compared to crosslinked cellulosic fibers that have not been treated with a whitening agent.

In one embodiment, the dyed crosslinked cellulosic fibers are then treated with one or more bleaching agents to provide a crosslinked cellulosic fibers having further improved color.

The bleaching agent is applied to the dye-treated crosslinked cellulosic fibers. In one embodiment, the bleaching agent is hydrogen peroxide. In another embodiment, the bleaching agent is a combination of hydrogen peroxide and sodium hydroxide. Other suitable bleaching agents include peroxy acids (e.g. peracetic acid), sodium peroxide, chlorine dioxide, sodium chlorite, and sodium hypochlorite. Mixtures of bleaching agents may also be used.

The dyed crosslinked cellulosic fibers can be advantageously treated with from about 0.045 kg hydrogen peroxide per air-dried meteric ton fiber (0.045 kg/admt) to about 9.1 kg hydrogen peroxide/admt fiber. In one embodiment, the fibers are treated with from about 0.045 kg hydrogen peroxide/admt fiber to about 4.6 kg hydrogen peroxide/admt fiber. In another embodiment, the fibers are treated with from about 0.045 kg hydrogen peroxide/admt fiber to about 4.6 kg hydrogen peroxide/admt fiber.

In the method, the bleaching agent is applied to the dyed crosslinked fibers after curing during the remoisturizing stage before the baling.

There are various methods by which the crosslinked cellulosic fibers may be contacted with the bleaching agent (e.g., hydrogen peroxide and sodium hydroxide). In one embodiment, the fibers are contacted after being discharged from the curing tower. The amount of alkaline solution and bleaching agent preferably utilized is dependent

upon the particular agents used and the reaction conditions. In one embodiment, the fibers are contacted after curing and during remoisturization. The sodium hydroxide can be added at the suction of the remoisturization pump and the hydrogen peroxide can be added just before the re-moisturization spray nozzle as the mixture enters the fiber stream, as described in U.S. Patent No. 5,562,740, incorporated herein by reference in its entirety.

The color properties (L, a, b, Whiteness Index) of the whitened crosslinked fibers of the invention are compared to dyed crosslinked fibers and control fibers (i.e., crosslinked fibers that are untreated and crosslinked fibers treated only with bleaching agent) and the results summarized in Table 1.

In Table 1, the cellulosic fibers were CF416 fibers (commercially available from Weyerhaeuser Company, Federal Way, WA) that were treated with citric acid (about 7.6 percent by weight based on the total weight of dry fibers), sodium hypophosphite (about 0.68 percent by weight based on the total weight of dry fibers, and the amount of dye (Pergasol Blue NLF (Blue NLF) and Pergasol Blue PTD (Blue PTD)), as indicated and then cured at about 180°C for about 5 minutes. Bleaching agents (sodium hydroxide and hydrogen peroxide) were then applied to the dyed crosslinked fibers in the indicated amounts.

To illustrate the principles of the invention, a discussion of whiteness and brightness is useful. *Webster's Dictionary* defines white as "the object color of greatest lightness characteristically perceived to belong to objects that reflect diffusely nearly all incident energy throughout the visible spectrum". Used as a noun or adjective, white is defined as "free from color". Most natural and many man-made products are never "free from color". Whether the "white" product is fluff pulp, paper, textiles, plastics, or teeth, there is almost always an intrinsic color, other than white, associated with it. Consider two hypothetical objects. The first meets Webster's definition of white: one characterized by a flat spectrum of high reflectance and a second, which is the first with a small amount of blue colorant added (resulting in an unequal spectrum). Most people will judge the second to be whiter, even though its total reflectance is lower in certain spectral regions. The first will be judged as a "yellow-white" while the second a "blue-white". Further, with the subjectivity of human color vision certain associations are unconsciously made. Blue-white is associated with "clean and pure", while

"yellow-white" denotes "dirty, old or impure". Consequently, the types and amounts of fillers and colorants, which hues are appropriate (e.g., red-blue, green-blue), and the optimal optical prescription to target have been the subject of considerable interest.

Whiteness attribute, not TAPPI brightness, better correlates with customer preference for product whiteness. When people are given a choice between two products having equal TAPPI brightness, usually the product exhibiting the higher whiteness attribute is preferred. The application of CIE Whiteness is but one measure of such a whiteness attribute. Similarly, a product having higher whiteness than the product to which it is being compared is preferred even when the former exhibits a lower brightness. TAPPI Brightness in North America and ISO Brightness throughout the rest of the world, are pulp and paper industry-specific standards used to loosely quantify the "whiteness" of a product. Regardless of which standard is applied, TAPPI or ISO, brightness is defined as the percent reflectance of product measured at an effective wavelength of 457 nm. In general, higher brightness is perceived by the industry to imply higher whiteness, but this is not always the case. Because brightness is a band-limited measurement taken in the blue end of the visible spectrum, it essentially measures how blue a product is. If a brightness specification is relied on, it is possible to maximize TAPPI brightness, yet produce a product that appears blue, not white. Brightness provides little indication of how white a product is nor does it tell anything about its lightness, hue, or saturation. As a whiteness specification, it is insufficient. Such is the danger of pursuing brightness when whiteness is the principal objective.

L, *a*, and *b* are used to designate measured values of three attributes of surface-color appearance as follows: *L* represents lightness, increasing from zero for black to 100 for perfect white; *a* represents redness when positive, greenness when negative, and zero for gray; and *b* represents yellowness when positive, blueness when negative, and zero for gray. The concept of opponent colors was proposed by Hering in 1878. Since the 1940s, a number of measurable *L, a, b* dimensions have been defined by equations relating them to the basic CIE XYZ tristimulus quantities defined in CIE Document No. 15. Measured values for a given color will depend on color space in which they are expressed [(TAPPI T 1213 sp-98 "Optical measurements terminology (related to appearance evaluation of paper")].

Basic color measurement is made using commercially available instruments (e.g., Technibrite MicroTB-1C, Technydine Corp.). The instrument scans through the brightness and color filters. Fifty readings are taken at each filter position and averaged. The measurements are reported as Brightness, R(X), R(Y), and R(Z). Brightness is ISO brightness (457 nm), R(X) is absolute red reflectance (595 nm), R(Y) is absolute green reflectance (557 nm), and R(Z) is absolute blue reflectance (455 nm). The CIE tristimulus functions X, Y, and Z are then computed in accordance with the following equations: $X = 0.782\ R(X) + 0.198\ R(Z)$, $Y = R(Y)$, and $Z = 1.181\ R(Z)$. Next *L, a* and *b* values are computed using the established equations (Technibrite Micro TB-1C Instruction Manual TTM 575-08, Oct. 30, 1989). Whiteness Index, $WI_{(CDM-L)}$, was calculated according to the equation, $WI_{(CDM-L)} = L - 3b$, according to TAPPI T 1216 sp-98 (TAPPI T 1216 sp-98 "Indices for whiteness, yellowness, brightness and luminous reflectance factor").

The Whiteness Index and Hunter color values for the crosslinked fibers are presented in Table 1. Color (Hunter *L*, *a*, *b)* and Whiteness Index (WI) are provided as initial values, values after one, seven, and fourteen days.

TABLE 1. EFFECT OF BLUE DYE AND BLEACH ON CROSSLINKED FIBER WHITENESS.

	Dye	NaOH	H_2O_2	L				a				b				Whiteness Index			
Dye	g/ admt	kg/ admt	kg/ admt	0	1	7	14	0	1	7	14	0	1	7	14	0	1	7	14
–	0	0	0	94.1	94.8	95.1	95.1	-1.44	-1.51	-1.60	-1.54	9.53	8.72	8.61	8.55	65.5	68.6	69.3	69.4
–	0	0.91	0.45	95.0	95.7	96.0	95.8	-1.95	-1.77	-1.83	-1.77	9.30	7.62	7.31	7.26	67.1	72.8	74.1	74.1
Blue NLF	28.4	0	0	94.5	94.9	95.1	95.3	-1.87	-1.83	-1.71	-1.67	8.50	7.07	7.17	6.22	69.0	73.7	73.6	76.6
Blue NLF	28.4	0.91	0.45	94.6	95.4	95.5	95.6	-2.12	-1.90	-1.50	-1.74	9.17	6.53	5.38	5.96	67.1	75.8	79.4	77.7
Blue NLF	56.7	0	0	93.5	93.7	93.9	94.0	-1.98	-1.99	-1.98	-1.86	8.53	7.83	7.92	7.18	67.9	70.2	70.2	72.5
Blue NLF	56.7	0.91	0.45	94.2	94.7	95.0	94.8	-2.12	-1.93	-1.75	-1.80	7.83	6.20	5.52	5.60	70.7	76.1	78.4	78.0
Blue PTD	28.4	0	0	93.1	93.7	93.8	93.7	-1.31	-1.20	-1.19	-1.45	8.28	7.14	6.52	5.91	68.3	72.2	74.3	76.0
Blue PTD	28.4	0.91	0.45	93.3	93.7	93.7	93.8	-1.66	-1.48	-1.32	-1.22	6.66	5.54	4.64	4.17	73.3	77.1	79.8	81.3
Blue PTD	56.7	0	0	92.0	92.4	92.6	92.3	-0.99	-0.78	-0.65	-0.92	6.83	5.87	4.93	4.27	71.5	74.8	77.8	79.5
Blue PTD	56.7	0.91	0.45	91.7	92.1	92.2	92.2	-1.12	-0.97	-0.40	-0.80	4.86	4.08	2.22	3.27	77.2	79.9	85.5	82.4

Referring to Table 1, the addition of dye alone reduces Hunter *b* (yellowness) and improves whiteness. Bleaching of dyed crosslinked fibers further enhances whiteness. Both dyes appear to lower Hunter *b*, and a greater decrease is observed for Blue PTD. Bleaching further decreases Hunter *b* for the dyed fibers. Synergy between the dye and bleaching is apparent at the 2 oz level at day 0, 1, and 7. Regarding Whiteness Index, the dyed fibers have improved Whiteness Index compared to control fibers. Bleaching further enhances Whiteness Index of dyed fibers.

Increased grayness (a reduction in *L*) is frequently observed with the addition of dyes and is undesirable. The Blue NLF is unexpectedly effective in reducing Hunter *b* (yellowness) without a corresponding reduction in Hunter *L*. Addition of bleach to the NLF dyed material further lowers *b* and further improves the Whiteness Index.

The whitened crosslinked cellulosic fibers of the invention can be advantageously incorporated into a variety of products, including, for example, paper boards, tissues, towels, and wipes, and personal care absorbent products, such as infant diapers, incontinence products, and feminine care products. Thus, in another aspect, the invention provides absorbent products including wipes, towels, and tissues as well as infant diapers, adult incontinence products, and feminine hygiene products that include bleached polyacrylic acid crosslinked cellulosic fibers.

While the preferred embodiment of the invention has been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention.